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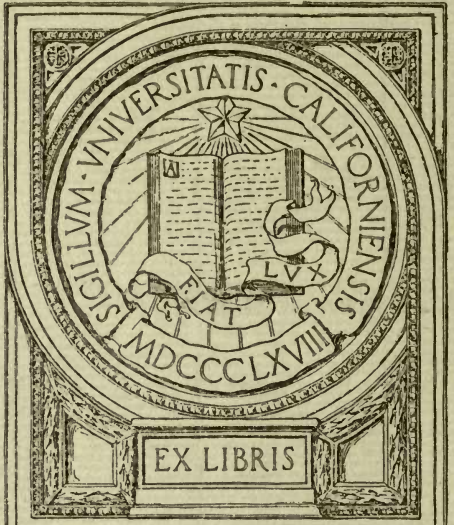

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Mercuri-Organic Derivatives

I. The Mercurization of Aromatic Amines and Its Relation to the Theory of Substitution.

II. A Study of the Nitranilines. Determination of the Position of the Mercury in the Mercurized Nitranilines.

A DISSERTATION

SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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ISADORE MEYER JACOBSOHN

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Reprinted from the Journal of the American Chemical Society, Vol. XLIII, No. 8, August, 1921 and Vol. XLIV, No. 4, April, 1922.

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MERCURI-ORGANIC DERIVATIVES. THE MERCURIZATION OF AROMATIC AMINES AND ITS RELATION TO THE THEORY OF SUBSTITUTION.[1]

The principles underlying the mercurization of aromatic compounds have occupied the attention of one of us (Kh.) for the past two years. The important fact that, in a mono-substituted benzene derivative, the mercury enters *para* or *ortho* to the group already present in the molecule, was pointed out early by Dimroth,[2] and has been substantiated by the vast amount of experimental work done by others. This fact of *ortho* and *para* substitution is particularly striking when one attempts to apply the theories of substitution to mercurization since mercury never enters *meta* to the group already present in the molecule. Even where the usual rules of substitution require that a *meta* derivative be formed, *e. g.*, with benzoic acid, benzophenone, and nitrobenzene, only *ortho* substituted mercury compounds have been isolated.

The phenomenon of mercurization was considered by Dimroth to be similar to that of nitration, sulfonation, etc., in the sense that the position taken by the entering mercury in compounds containing groups now considered electro-negative, *e. g.*, amino or hydroxyl groups, was quite in agreement with the rule of Crum Brown and Gibson. He considered the exceptional behavior of nitrobenzene, benzoic acid, and benzophenone as anomalous reactions which needed to be accounted for. However, until recently, no effort has been made to explain the orientation of mercury in the benzene molecule.[3] The rule of Crum Brown and Gibson, being purely empirical, offers no suggestion as to the mechanism of the reaction, nor does it help to predict whether a compound could be mercurized or not. Therefore, it appeared desirable to apply some of the modern theories of substitution to the orientation of mercury in the benzene molecule.

In the present paper, the authors will confine themselves to the mechanism of mercurization of aromatic amines and also attempt to show that the mechanism suggested for mercurization may be extended to explain sat-

[1] This work was carried out in coöperation with Dr. M. S. Kharasch and was published in *J. Am. Chem. Soc.*, **43**, 1894 (1921), in an article by M. S. Kharasch and I. M. Jacobsohn.

[2] Dimroth *Ber.*, **35**, 2853 (1902).

[3] Schoeller, Schrauth, and Liese (*Ber.*, **52B**, 1777 (1919) apply the theory of Armstrong for substitution in aromatic amines to mercurization, the limitations of which theory will be pointed out later.

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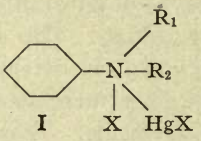
isfactorily orientation of other groups in the case of aromatic amines. It will be shown further, in a condensed critical survey of the theories of others, that none of these is completely satisfactory. For example, most of them fail to account for the fact that dimethylaniline is mercurized readily.

The theory which the present authors have been led to adopt as a result of their extended experimental work, briefly stated, is as follows. The mercurization of an aromatic amine proceeds in two stages: first, the formation of an ammonium salt with the mercuric acetate or chloride to give a compound of the general type I.



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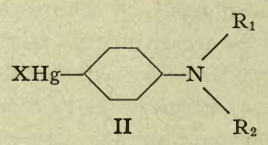


II

This compound is then rearranged to the more stable configuration having the mercury radical attached to carbon, (Type II), the *para* position being usually favored.[4] If this position is already occupied, the mercury goes to the *ortho* position. Furthermore, it is only the ammonium salt that undergoes rearrangement,[5] the instability of the salt being due to the presence of an electropositive group or atom on the amino nitrogen.[6]

This, it will be noted, is the application to mercurization of the theories of substitution of Armstrong,[7] Bamberger,[8] Chattaway[9] and others, and of the general theory of catalysis advanced by Stieglitz,[10] Acree[11] and others

[4] The fact of rearrangement may be due to a smaller energy content on the part of the rearranged compound. This relationship was shown to hold by Rother and Stoermer (*Ber.*, **46**, 260 (1913)) for a number of compounds, *e. g.*, cinnamic acid and the isomeric allocinnamic acid.

[5] Acree and Johnson, *Am. Chem. J.*, **38**, 265 (1905), have demonstrated that, in the rearrangement of N-chloro-acetanilide, it is the salt and not the free base that rearranges. They fail, however, to attach any importance to the positive charge on the rearranging group, a fact which has already been pointed out by Stieglitz and Stagner, *J. Am. Chem. Soc.*, **38**, 2057 (1916).

[6] Acree and Johnson, *Am. Chem. J.*, **38**, 265 (1905), have shown that, when N-chloro-acetanilide is treated with hydrogen bromide, the speed of the rearrangement is a thousand times greater than when hydrogen chloride is used, and that the end product of the rearrangement is *p*-bromo-acetanilide, instead of *p*-chloro-acetanilide.

[7] Armstrong, *J. Chem. Soc.*, **51**, 258, 583 (1887).

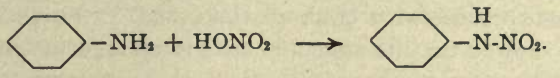
[8] Bamberger, *Ber.*, **27**, 586 (1894).

[9] Chattaway, *J. Chem. Soc.*, **75**, 1048 (1899).

[10] Stieglitz, *Proc. Congress of Arts and Sci.* (St.Louis), **IV**, 278(1904); *Am. Chem. J.*, **39**, 29 (1908).

[11] Acree, *ibid.*, **37**, 410 (1907).

that acid catalysts act through salt formation.[12] However, the theory advanced by the present authors diverges from that of Armstrong, Bamberger, and Chattaway, and also from recent theory of mercurization of Schoeller, Schrauth and Liese[3] in a few very important aspects. The theories advanced by the above mentioned authors assume that the entrance of a group into the nucleus of an aromatic amine is always preceded by substitution on the amino nitrogen, thus,



However, as an explanation, this is not adequate to account for the mechanism of substitution of tertiary amines, of the type of dimethyl aniline which contains no replaceable hydrogen. Furthermore, they do not emphasize the nature and importance of the catalysts used in substitution, *i. e.*, strong acids. That the rôle played by acid catalysts is that of salt formation has been pointed out very clearly by Stieglitz[10] in his work on the catalysis of imido-esters, as well as by Acree.[11]

We find thus, that the previous hypotheses have to be modified, if they are to explain consistently all the facts of substitution without further assumptions. The hypothesis advanced by the writers to explain the mercurization of aromatic amines lends itself admirably to this purpose. We shall now proceed to illustrate as briefly as possible the basis for this hypothesis and then show that it is quite compatible with the *ortho* and *para* orientation of other groups in the case of aromatic amines.

That mercury has a great affinity for amino nitrogen and for carbon is best illustrated by the readiness with which the mercury-ammonium complexes are formed, and by the great stability of mercury-carbon compounds.[13] It is the combination of this property of mercury to form stable nitrogen and carbon compounds, and the relatively greater stability of the latter, which enables us to attach mercury to the carbon of the benzene ring in the case of aromatic amines.

Within the scope of a series of investigations being carried out by the one of us, work was undertaken upon the mercurization of the N-alkylated nitro-anilines. It was found that mercurization does not take place when *p*-nitro-dimethylaniline is treated with mercuric acetate in alcoholic solution. Though various experimental conditions were tried, the

[12] In this connection, the work of Reilly and Hickinbotham (*J. Chem. Soc.*, **117**, 103 (1919)) on the rearrangement of *n*-butylaniline is quite significant. They found that only those salts which are capable of combining with the amino group effected the rearrangement.

[13] The stability of the mercury-carbon union is a relative term. It depends to a large extent upon the position of the mercury in the molecule and upon the nature of the neighboring groups. This will be discussed in a later paper. See also Stieglitz, Kharasch, and Hanke, *J. Am. Chem. Soc.*, **43**, 1186 (1921).

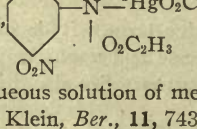
efforts were futile. It seemed, however, in view of the results of an investigation carried out with other nitro-anilines,[14] that mercurization should take place unless there was some property of the mercurizable nitro-anilines which was not shared by the *p*-nitro-dimethylaniline. Reference to the literature at once revealed the fact that *p*-nitro-dimethylaniline is an extraordinarily weak base. It is precipitated from even conc. hydrochloric acid solution as the free base instead of its hydrochloride, and it does not combine with chloroplatinic acid.[15] Further reference to the literature showed that its *ortho* and *meta* isomers form salts more readily. An investigation of the reactions of these isomers with mercuric acetate showed not only that the reactions are completed within a very short time but at a comparatively low temperature. An attempt was then made to mercurize *p*-nitro-diethylaniline. This met with the same failure as that of the corresponding dimethyl derivative. That this failure to mercurize is not due simply to the fact that the *para* position is occupied was then demonstrated by the fact that *p*-nitro-monomethyl- and *p*-nitro-mono-ethylanilines are mercurized without difficulty, the mercury being oriented to the position *ortho* to the amino group.

These facts, taken in conjunction with the intermediates already isolated[16] and those obtained by Schoeller, Schrauth and Liese,[3] the complex salts of aromatic amines isolated by Klein[17] and the known general fact of the great affinity of mercury for an amino nitrogen, led us to adopt the hypothesis that mercurization proceeds first by the addition of the mercury salt to the amino group, *i. e.*, to form an ammonium salt. This ammonium salt then rearranges to a compound in which the mercuric radical is attached to carbon.[4]

From this theory of the mechanism of mercurization, one of the most logical deductions to be made is that, *of the aromatic amines, only those which are capable of forming salts will mercurize.* Among other tests, one to which this deduction has been put was an attempt to mercurize trimethyl-phenyl-ammonium acetate, a compound in which the formation of a double salt with the mercuric acetate used is impossible. This compound was not mercurized although a water suspension of dimethylaniline mercurizes within one or two minutes, with great evolution of heat.

[14] Unpublished work of Kharasch, Lommen, and Jacobsohn.

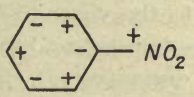
[15] We found, however, that a hydrochloride of *p*-nitro-dimethylaniline could be prepared by passing dry hydrogen chloride into a benzene solution of the base.

[16] Kharasch, Lommen, and Jacobsohn (unpublished work) have isolated the compound,  by treating an alcoholic solution of *m*-nitroaniline with an aqueous solution of mercuric acetate.

[17] Klein, *Ber.*, **11**, 743(1778).

The theory here advanced as to the mechanism of mercurization of aromatic amines adapts itself as already stated, quite readily to the explanation of the orientation of other groups upon substitution in the nucleus of aromatic amines.[18] Not only does it explain satisfactorily the cases of *ortho* and *para* substitution but, as will be shown later, it explains also the fact that a mixture of all three isomers is obtained when an aromatic amine is nitrated in conc. sulfuric acid solution, as well as the more recent observations of Vorländer[19] that, upon bromination and nitration, the quaternary ammonium salts yield only the *meta* derivative.

To explain these cases of *meta* substitution, Vorländer advances a theory of the benzene nucleus in which he assumes that the hydrogen atoms in the benzene molecule have positive tensions,[20] and that it is the tension within the nucleus which determines the position taken by the entering substituent. He assumes, further, that the nature of the tension on the group already substituted in the molecule exerts an influence on the arrangement of the tensions within the nucleus. Thus for nitrobenzene he assumes Structure I.



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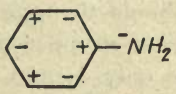

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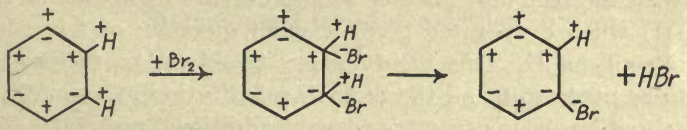
while, for aniline, Structure II is assumed. Further, substitution takes place by absorption with the subsequent loss of a molecule of acid or water[21] thus:



Vorländer makes the additional postulate, in order to explain the cases of *meta* substitution in aromatic amines, that, upon salt formation, there is a change in the tension throughout the molecule, *e. g.*, upon treating

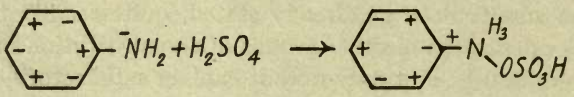
[18] It is self-evident that this theory is applicable also to such rearrangements as those of hydrazobenzene, diazo-aminobenzene, the Fischer and Hepp, etc. It is to be noted that, in all cases, where the rearranging compound is a weak base, the reaction must be carried out in the anhydrous media to insure salt formation.

[19] Vorländer, *Ber.*, **52B**, 263 (1919).

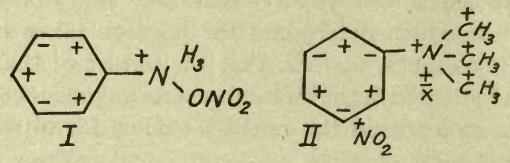
[20] In order to avoid committing himself to any theory as to the nature of valence, Vorländer uses the term "tension" and denotes the kind of tension by + and −. While he does not assume that they are electrical in nature, the properties assigned for them are such that, for the purpose of discussing substitution, there is little distinction to be made.

[21] It is rather peculiar that Vorländer does not take into account the fact that bromine is Br^+-Br^-, unless by an error in print, since the existence of positive bromine has been proved conclusively. (W. A. Noyes, *J. Am. Chem. Soc.*, **23**, 460 (1901); Stieglitz, *ibid.*, **23**, 796 (1901); Walden, *Z. physik. Chem.*, **43**, 385 (1903).

aniline with sulfuric acid, the following change is assumed to take place.



Such an assumption is entirely unwarranted. Not only are there no experimental facts upon which to base such an hypothesis, but the assumption made involves an upheaval taking place within the molecule, as well as a change of tension between the carbon and groups attached to it. Such a supposition as a change of tension would also demand that, in a compound such as aniline nitrate, analogous to aniline sulfate, the tension on the nitrogen bound to the phenyl group must be positive.



This compound should then, according to the views of Vorländer, give a *meta* derivative when dropped into conc. sulfuric acid. On the contrary, however, it gives only *o*- and *p*-nitro derivatives.[22] Similarly, the nitration of aromatic quaternary ammonium compounds demands, according to Vorländer, that the tension between the ammonium nitrogen and the carbon of the benzene nucleus be positive (II). This is hardly compatible with the fact that a water solution of the hydroxide of the compound (II) when evaporated gives a small quantity of trimethylamine and *m*-nitrophenol.[23] This theory must, therefore, be further modified if it is to be made to fit all the facts of substitution in aromatic amines.

Similarly, it has been necessary to make additional postulates to all previous theories in an attempt to build a workable theory of substitution. Yet, with all these postulates, none of the older theories can be made to fit all the facts of substitution. However, no new postulates need be made to the theory advanced by the present authors. Once it is assumed that all *ortho* and *para* substitution in the hydroquinoid nucleus of aromatic amines takes place through intermediate salt formation, it follows that, when such salt formation is impossible, as in the quaternary ammonium salts, substitution must take place in the *meta* position or, as in such special cases as that of mercurization, it is not accomplished at all.

Not only does the theory advanced explain the case of *meta* substitution in the quaternary ammonium salts, but it explains also the fact that a mixture of all three isomers is obtained upon nitration of an aromatic amine in conc. sulfuric acid solution. It explains, further, the fact that

[22] Bamberger, *Ber.*, **28,** 400 (1895).

[23] Staedel and Bauer, *ibid.*, **19,** 1939 (1885).

the yield of the *meta* derivative increases with the amount of sulfuric acid used. Here it will be seen that an equilibrium mixture of both the amine and the ammonium salt exists in such a solution. Therefore, in such a mixture both types of substitution, that dependent upon intermediate compound formation, giving *ortho* and para derivatives, and the substitution of a salt yielding a *meta* derivative, are found. Again, as the volume of sulfuric acid is increased, the equilibrium will be shifted to form more of the sulfate, thus increasing the yield of the *meta* derivative.

Furthermore, the theory here advanced also offers an explanation of certain peculiar facts of rearrangement. For example, the rearrangement of β-phenyl-hydroxylamine[24] in alcoholic solution with hydrogen chloride as catalyst, gives not only *p*-amino phenetole but also *p*-chloroaniline, the more strongly electro positive chlorine atom rearranging. The theory advanced predicts that N-substituted aromatic amines, when treated with a catalyst capable of being oxidized by the group already substituted in the molecule will yield a derivative having the more strongly electro positive group in the *para* position.

It will be seen, therefore, that the present theory explains from a single standpoint the rearrangement and substitution in the case of aromatic amines, without the necessity of any additional postulates. It is also far more adequate for the explanation of these facts and furnishes a more workable hypothesis than any of the other theories of substitution.

Experimental Part.

Method used for Mercurization.

The method used for the preparation of the compounds herein described is, briefly, as follows. One mol of the compound to be mercurized was dissolved in a small volume of alcohol and boiled with an aqueous solution containing 0.9 mol of mercuric acetate, until a test portion gave no black precipitate of mercuric sulfide when treated with ammonium sulfide. This reaction mixture was filtered hot. Upon cooling, the acetate of the mercurized compound crystallized from the solution.

The filtrate from the above was treated with an aqueous solution of sodium chloride, whereupon the chloride of the mercury compound soon precipitated. The total yield of mercurized product calculated upon the basis of the mercuric acetate used, was almost quantitative.

An Attempt to Mercurize *p*-Nitro-dimethylaniline and *p*-Nitro-diethylaniline.—As stated in the theoretical part, several attempts were made to mercurize *p*-nitro-dimethylaniline, all of which met with failure. The method above outlined was used, as well as several other methods, none of which yielded a mercurized product. Similarly, attempts to mercurize *p*-nitro-diethylaniline were without success.

***o*-Nitro-*p*-Acetoxymercuri-dimethylaniline, $(C_6H_3(1)N(CH_3)_2(2)NO_2(4)HgO_2C_2H_3.)$**—This compound was prepared from *o*-nitro-dimethylaniline and mercuric acetate.

[24] See, however, Stieglitz, *Am. Chem. J.*, 46, 327 (1911

The reaction was completed after half an hour's boiling. The reaction mixture was filtered hot in order to remove the small amount of mercurous acetate formed in the reaction. It was then cooled and the precipitate collected on a filter. The precipitate was then washed with alcohol, and dried to constant weight *in vacuo* over sulfuric acid.

Analyses. Subs., 0.2759: dry N_2, 16.20 cc. (22° and 741 mm.). Subs., 0.2604: HgS, 0.1427. Calc. for $C_{10}H_{12}O_4N_2Hg$; N, 6.61; Hg, 47.23. Found: N, 6.63; Hg, 47.26.

The compound thus obtained is bright yellow; m. p. 160°. It is crystalline, and is soluble in the common organic solvents.

***o*-Nitro-*p*-Chloromercuri-dimethylaniline.** ($C_6H_3(1)N(CH_3)(2)NO_2(4)HgCl.H_2O$).—This compound was washed well with water to remove sodium chloride and finally with alcohol, and dried *in vacuo* over sulfuric acid to constant weight.

Analyses. Subs., 0.2635: dry N_2, 15.60 cc. (21.5° and 741 mm.). Subs., 0.3233: AgCl, 0.1096. Calc. for $C_8H_{11}O_3N_2HgCl$: N, 6.69; Cl, 8.46. Found. N, 6.71; Cl, 8.38.

The substance is red and amorphous. It is soluble in acetone and in boiling alcohol. It melts at 185°, with decomposition.

***m*-Nitro - *p* - Acetoxymercuri - dimethylaniline,** ($C_6H_3(1)N(CH_3)_2(3)NO_2(4)HgO_2C_2H_3$).—This preparation was obtained upon treating *m*-nitro-dimethylaniline with mercuric acetate. A half hour's boiling was sufficient to carry the reaction to completion. For analysis, the compound was dried to constant weight over sulfuric acid.

Analyses. Subs., 0.2924: dry N_2, 17.05 cc. (20° and 734 mm.). Subs., 0.2940: HgS, 0.1610. Calc. for $C_{10}H_{12}O_4N_2Hg$:N, 6.61; Hg, 47.23. Found: N, 6.56; Hg, 47.23.

The compound is obtained in the form of brilliant orange needles. It is soluble in the common organic solvents; m. p. 140°.

***m*-Nitro - *p* - Chloromercuri-dimethylaniline,** ($C_6H_3(1)N(CH_3)_2(3)NO_2(4)HgCl$).—This compound was obtained from the filtrate of the preceding preparation.

Analysis. Subs., 0.3438: AgCl, 0.1237. Calc. for $C_8H_9O_2N_2HgCl$: Cl, 8.84. Found: 8.90.

The compound is red and amorphous. It is soluble in acetone and in boiling alcohol. It melts at 220°, with decomposition.

***p*-Nitro-*o*-Acetoxymercuri-monomethylaniline,** ($C_6H_3(1)NH.CH_3(4)NO_2(2)HgO_2C_2H_3$).—This compound was prepared from *p*-nitro-methylaniline and mercuric acetate. The product obtained was extracted with ether in order to remove unchanged *p*-nitro-methylaniline, and the residue was recrystallized from alcohol. A dark red solid remained which was insoluble in alcohol, but the quantity was too small to be analyzed.

Analyses. Subs., 0.2585: dry N_2, 15.6 cc. (21° and 736 mm.). Subs., 0.2981: HgS, 0.1673. Calc. for $C_9H_{10}O_4N_2Hg$: N, 6.84; Hg, 48.82. Found: N, 6.79; Hg, 48.38.

The compound forms small yellow crystals melting at 197° with decomposition. It is soluble in acetone and in hot alcohol to which a few drops of glacial acetic acid have been added. When treated with a conc. potassium hydroxide solution, a brick-red compound is formed. Upon dilution, the compound again becomes yellow.

***p*-Nitro-*o*-Chloromercuri - monomethylaniline,** ($C_6H_3(1)N.H.CH_3(4)NO_2(2)HgCl-H_2O$).—This compound is obtained from the filtrate of the preceding compound.

Analysis. Subs., 0.2972: AgCl, 0.1036. Calc. for $C_7H_9O_3N_2HgCl$: Cl, 8.75. Found: 8.62.

The compound is yellow and crystalline. It is soluble in acetone and in boiling alcohol. It melts at 215°, with decomposition.

The position of the mercury in this compound was determined by the method of Dimroth.[25] The acetate was treated with two equivalents of a solution of potassium perbromide. The product was then extracted with ether and the extract purified from alcohol; m. p. 112–113°. When mixed with 4-nitro-2,6-dibromo-monomethylaniline, prepared by the method of Blanksma,[26] the melting point was not lowered. The use of only one molecule of the bromine in solution yielded no definite compound. Since the position could not be thus in dispute the dibromo derivative was therefore isolated.

p-Nitro-*o*-Acetoxymercuri-mono-ethylaniline, $(C_6H_3(1)N.H.C_2H_5(4)NO_2(2)Hg.O_2C_2H_3)$.—This compound was prepared from *p*-nitro-mono-ethylaniline, and was purified from the unchanged raw material by recrystallization from alcohol.

Analyses. Subs., 0.2641: dry N_2, 15.7 cc. (24.5° and 731 mm.). Subs., 0.3480; HgS, 0.1912. Calc., for $C_{10}H_{12}O_4N_2Hg$: N, 6.61; Hg, 47.23. Found: N, 6.56; Hg, 47.17.

It crystallizes from alcohol in small yellow crystals; m. p. 183°. It is also soluble in acetone. When treated with conc. potassium hydroxide solution, a brick-red compound is obtained. Dilution of the solution restored the original yellow color.

p-Nitro-*o*-Chloromercuri-mono-ethylaniline, $(C_6H_3(1)N.H.C_2H_5(4)NO_2(2)HgCl.H_2O)$.—The compound was prepared in the usual manner. It is obtained in the form of an amorphous yellow solid; m.p. 218°, with decomposition. For analysis it was dried to constant weight over sulfuric acid.

Analysis. Subs., 0.4544: AgCl, 0.1573. Calc. for $C_8H_{11}O_3N_2HgCl$: Cl, 8.46; Found: 8.56.

It is soluble in acetone and in hot alcohol.

The position of the mercury in this compound was determined by the method used above for the corresponding methyl derivative. The melting point of the 4-nitro-2,6-dibromo-ethylaniline thus obtained was 68–71°. The melting point was not lowered when a mixture of the compound with known 4-nitro-2,6-dibromo-ethylaniline was used.

p-Nitro-*o*-Bromo-mono-ethylaniline, $(C_6H_3(1)N.H.C_2H_5Br(4)NO_2)$.—This compound was prepared by the addition of a solution of bromine in glacial acetic acid to a solution of an equivalent portion of *p*-nitro-mono-ethylaniline in the same solvent. After standing for about half an hour, the reaction mixture was diluted with water, and the precipitated compound collected on a filter. It was washed with water and a little alcohol. After crystallization from alcohol, the compound was dried to constant weight *in vacuo*. Yield, 90%.

Analysis. Subs., 0.2704: dry N_2, 26.50 cc. (17° and 750 mm.). Calc. for $C_8H_9O_2N_2Br$: N, 11.44. Found: 11.39.

The compound crystallized from alcohol in beautiful long yellow prisms which are highly refractive; m.p. 65° to 66°. It is insoluble in water but soluble in all common organic solvents.

When an alcoholic solution of the compound is treated with conc. potassium hydroxide solution, the alcoholic layer assumes a red color. Upon evaporation of the alcohol, or upon dilution with water, the yellow compound is again obtained.

p-Nitro-*o*-Dibromo-mono-ethylaniline, $(C_6H_2(1)N.H.C_2H_5(2,6)Br_2(4)NO_2)$.—This compound was prepared in the same manner as the above monobromo derivative, in this case, with two mols of bromine. For analysis the compound was crystallized from alcohol. Yield, 90%.

Analysis. Subs., 0.2761: dry N_2, 21.2 cc. (21° and 744 mm.). Calc. for $C_8H_8O_2N_2Br_2$: N, 8.68. Found: N, 8.74.

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[25] Dimroth, *Ber.*, **35**, 2033 (1902).

[26] Blanksma, *Rec. trav. chem.*, **31**, 271 (1902).

This compound crystallized from alcohol in small yellow needles; m.p. 75–76°. It is insoluble in water, but soluble in all common organic solvents.

Upon treatment with a conc. potassium hydroxide solution, an alcoholic solution of the compound turns red. If the alcohol is evaporated, or the solution diluted with water, the color is restored to the original yellow.

An Attempt to Mercurize Trimethyl-phenyl-ammonium Acetate.—A solution of 0.5 mol of mercuric acetate was added to a solution of trimethyl-phenyl-ammonium acetate. Even after standing for two months at room temperature, no mercurized product could be isolated. The solution gave a heavy precipitate of mercuric sulfide when treated with hydrogen sulfide.

Upon boiling another portion of the solution for 24 hours, no change was observed. A heavy precipitate of mercuric sulfide was again obtained upon treatment with hydrogen sulfide.

Summary.

1. A theory of the mercurization of aromatic amines has been advanced, postulating that mercurization is preceded by addition of a mercuric salt to the amino nitrogen, with the subsequent rearrangement of the mercury to the *ortho* or *para* position. This theory, without any additional postulates, has been shown to apply equally well to the introduction of other groups in the benzene nucleus in the case of aromatic amines.

2. This theory has been shown to apply also to rearrangements such as that of Fischer and Hepp, the nitro-amines, sulfamic acids, etc.

3. The limitations to other theories of substitution have been pointed out.

4. The preparation of mercury derivatives of *p*-nitro-methylaniline, *p*-nitro-ethylaniline, *o*-nitro-dimethylaniline, and *m*-nitro-dimethylaniline, and the preparation of *o*-bromo and *o,o*-dibromo-*p*-nitro-ethylanilines have been described.

A STUDY OF THE NITRANILINES.[1] DETERMINATION OF THE POSITION OF THE MERCURY IN THE MERCURIZED NITRANILINES.

The purpose of this investigation was to determine the positions which mercury takes upon introduction into the benzene nucleus of the three isomeric nitranilines. It was found that the positions taken by the mercury in the nitro-anilines is always *ortho* or *para* or *ortho-para* to the amino group.[2] This was established by preparing the acetyl derivatives of the various mercurized products, and subsequent replacement by bromine. The bromo derivatives were then compared with the respective synthetic products, prepared by other methods, and were found not to depress their melting points.

It was found, in all cases, that the positions taken were in perfect agreement with those demanded by the theory outlined in the preceding paper.

o-Acetoxymercuri-acetyl-*p*-nitro-aniline. $[C_6H_3(1)NH\cdot(CO\cdot CH_3)(4)NO_2(2)HgO.\text{-}OC_2H_3]$.—To prepare this compound 4 g. of *o*-acetoxymercuri-*p*-nitro-aniline was boiled under a reflux condenser with 10 cc. of acetic anhydride and 30 cc. of ethyl acetate. After a short time the solid was completely dissolved. The solution was then filtered hot, and upon cooling a white crystalline product separated. This was collected on a filter and washed with alcohol. Yield, 50%.

The compound is white and crystalline. It is soluble in ethyl acetate. With sodium hydroxide it gives no color change.

Determination of the Position of the Mercury in the Mercurized *p*-Nitro-aniline

The position of the mercury in the mono-mercury-substituted *p*-nitro-aniline was determined in the following manner. One mol of *o*-acetoxymercuri-acetyl-*p*-nitro-aniline was treated with 1 mol of potassium perbromide solution and the whole shaken until the color of the bromine had disappeared. The solid product of the reaction was collected on a filter and washed with water. It was then extracted with ether, the ethereal extract was evaporated to dryness, and the residue was recrystallized from hot water; m. p. 130°. When mixed with *p*-nitro-*o*-bromo-acetanilide prepared by synthetic methods, the melting point was not lowered. The position of the mercury is thus established as *ortho* to the amino group.

To determine the position of the mercury in the dimercury-substituted *p*-nitro-aniline the compound was first acetylated, in ethyl acetate suspension with acetic

[1] This work was carried out in coöperation with Dr. M. S. Kharasch and was included in a paper published in *J. Am. Chem. Soc.* **44**, 793 (1922), by M. S. Kharasch, F. W. M. Lommen, and I. M, Jacobsohn.

[2] It is of considerable interest, in this connection, that in the case of the dimercury compound of *m*-nitro-aniline the positions taken by the mercury are 2,4 ($NH_2=1$, $NO_2=3$) and not 4,6 as one might expect.

anhydride. The reaction was considered complete when the whole became almost white.[3] The acetylated compound thus obtained was treated with two mols of potassium perbromide in a manner similar to that used for the monomercury substituted derivative. A product was obtained which melted at 225–227°. When mixed with 4-nitro-2,6-dibromo-acetanilide the melting point was not lowered. The position of the mercury is thus established as being in the 2,6 positions ($NH_2 = 1$).

p-**Acetoxymercuri-diacetyl-*o*-nitro-aniline,** $[C_6H_2(1)N(CO\cdot CH_3)_2(2)NO_2(4)HgO\cdot OC_2H_3]$.—This compound was prepared from *p*-acetoxymercuri-*o*-nitro-aniline, using the same procedure as that already used for the preparation of the corresponding *p*-nitro-aniline derivative. The reaction in this case was found to take place much more slowly. For analysis the compound was dried *in vacuo* to constant weight.

Analysis. Subs., 0.2654: 13.8 cc. of dry N_2 (22° and 737.0 mm.). Calc. for $C_{12}H_{11}O_6N_2Hg$: N, 5.84. Found: 5.87.

The compound is of a straw-yellow color. It is soluble in sodium hydroxide solution imparting to the solution a yellow coloration. M. p. 194° with decomposition.

p-**Acetoxymercuri-acetyl-*o*-nitro-aniline,** $[C_6H_2(1)N\cdot H\cdot CO\cdot CH_3)(2)NO_2(4)HgO\cdot OC_2H_3]$.—To prepare this compound, a water suspension of *p*-acetoxymercuri-diacetyl-*o*-nitro-aniline was treated with a dilute solution of sodium hydroxide. The compound dissolved, giving the solution a yellow color. The solution was then filtered immediately into dil. acetic acid. A yellow crystalline precipitate formed immediately. This was collected on a filter and washed with water and alcohol. For analysis the compound was dried *in vacuo* over sulfuric acid to constant weight.

Analysis. Subs., 0.2835: 16.42 cc. of dry N_2 (20° and 737.2 mm.). Calc. for $C_{10}H_{10}O_5N_2Hg$: N, 6.40. Found: 6.55.

The compound is yellow and crystalline. It dissolves in sodium hydroxide, forming a yellow solution. After a short time this solution yields a red precipitate, further de-acetylation having taken place. It melts with decompositon at 194°.

Determination of the Position of the Mercury in the Mercurized *o*-Nitro-aniline Derivative

To determine the position of the mercury in the mercury derivative, the diacetyl compound was treated with potassium perbromide in the same manner as already described for the corresponding *para* compound. A lemon colored compound was obtained which, when recrystallized from water, melts at 104°. When mixed with some known *o*-nitro-*p*-bromo-acetanilide the melting point was not lowered. The mercury is shown thus to be in the position *para* with respect to the amino group.

p-**Acetoxymercuri-acetyl-*m*-nitro-aniline,** $[C_6H_3(1)NH\cdot(COCH_3)(3)NO_2(4)HgO\cdot OC_2H_3]$.—This compound was prepared from *p*-acetoxymercuri-*m*-nitro-aniline in the same manner as that described for the *p*-nitro-aniline derivative above. For analysis it was dried *in vacuo* over sulfuric acid to constant weight.

Analysis. Subs., 0.2522: 14.24 cc. of dry N_2 (18° and 739.5 mm.). Calc. for $C_{10}H_{10}O_5N_2Hg$: N, 6.40. Found: 6.45.

This compound is white. It melts with decomposition at 230°.

Determination of the Position of the Mercury in the Mercurized *m*-Nitro-aniline

The method of procedure used in determining the position of the *m*-nitro-aniline derivatives was similar to that used for the *para* compound. The compound obtained

[3] The compound thus obtained was insoluble in the common organic solvents and, owing to the presence of an appreciable quantity of metallic mercury formed in the course of the acetylation, was not analyzed.

when recrystallized from water melted at 135–139°. When mixed with some known *p*-bromo-*m*-nitro-acetanilide the melting point was not lowered. The position of the mercury is thus shown to be *para* to the amino group.

To determine the position of the mercury in the dimercury-substituted *m*-nitro-aniline, the latter compound was suspended in ethyl acetate and boiled under a reflux condenser with acetic anhydride until the whole became white.[4] The acetyl derivative thus prepared was treated with 2 mols of potassium perbromide, in the manner previously described. The product obtained was then filtered, dried and extracted with ether. The ethereal extract was evaporated to dryness, leaving a residue of melting point 141–146°. Upon recrystallization from 50% alcohol it melted at 150°. When mixed with known 2,4-dibromo-3-nitro-acetanilide the melting point was not lowered. The compound was then de-acetylated with conc. sulfuric acid at 120°. Upon dilution of this reaction mixture with water, a yellow product melting at 84–87° was obtained. Upon recrystallization from 50% alcohol, a product melting at 89° was obtained. When mixed with known 2,4-dibromo-3-nitro-aniline, the melting point was not lowered. This identifies the position of the mercury as being 2,4 with respect to the amino group (NO_2=3).

[4] In the course of the reaction, an appreciable amount of metallic mercury was formed. Since the compound thus obtained is insoluble in the common organic solvents, it could not be purified, and therefore was not analyzed.

In conclusion, the writer takes pleasure in acknowledging gratefully his appreciation of the sympathetic encouragement and personal kindness which Dr. M. S. Kharasch has shown him in the guidance of his work.

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